

blows is rather complicated, and it is difficult to deduce from the results anything more than the general conclusion stated above, that the wire is substantially elastic up to stresses much beyond the static elastic limit, and that the mathematical theory gives correct results. I hope, however, by suitable modifications of the experiment, to simplify the conditions, and obtain by this method more detailed information as to the properties of materials when subjected to shock. It seems to me quite possible that the stress-strain relations for stresses beyond the elastic limit may be much simplified if the stresses are applied for exceedingly short times, because the complication of hardening, due to over-straining, will be to a large extent removed.

“Phosphorescence caused by the Beta and Gamma Rays of Radium.” By G. T. BEILBY. Communicated by Professor LARMOR, Sec. R.S. Received January 25,—Read February 9, 1905.

1. Various observers have noticed that barium platino-cyanide, after continued exposure to the rays from radium, becomes brown or red, while the phosphorescence excited by the rays falls off considerably.* The following observations were made with the object of ascertaining the conditions under which this change occurs.

2. A specimen of Merck's barium platino-cyanide was recrystallized and obtained in prisms from 3 to 5 mm. long. The crystals were bright canary yellow and showed a pale blue fluorescence by obliquely reflected light.

3. The radium used was 30 milligrammes of pure bromide contained in a cell with a thin mica cover. This radium is the property of Mr. Frederick Soddy, to whom I am much indebted for granting me its exclusive use for more than three months. All the experiments were made without removing the mica cover of the cell, so that the effects produced were due entirely to the β and γ rays. In comparing the phosphorescence at different stages, black paper was interposed between the cell and the substance so as to cut off the luminous rays from the radium.

4. When yellow crystals of platino-cyanide are left on the mica cover of the radium cell for half an hour, the beginnings of the colour change from yellow to red are distinctly visible. In one hour those surfaces most directly in the path of the rays become strongly reddened. In eight hours the phosphorescence has fallen to a minimum of 8/100 of its original amount, at which it remains, however long the exposure may be continued.

Crystals were exposed to the rays for eight days, but the phosphor-

escent value did not further diminish, though the colour became rather deeper.

5. When the reddened crystals are removed from the action of the rays they at once cease to phosphoresce. At the outset, therefore, there are two well-marked characteristics in the behaviour of the platino-cyanide. (1) The phosphorescence starts at a maximum value which rapidly falls to $1/12$ or thereby; and (2) there is no after phosphorescence.

6. Other observers have stated that platino-cyanide screens which have been reddened by over-exposure to radium rays may be restored to the sensitive state by exposure to sunlight.* I have exposed reddened crystals on a glass plate to a condensed beam of sunlight for several hours without being able to observe any restoration of colour or phosphorescent quality. The observations here recorded seem to suggest that the restorative effect of sunlight, where it has been observed, must have been due to some conditions supplied by the other materials of which the screen was composed. The present observations show that the red crystals retain their new character over a period of many weeks either in the dark or in diffused daylight, and none of these observations have given any indication that the change is other than permanent.

7. The only way *completely* to restore the red crystals to the yellow state is by solution in water and recrystallisation. The properties of the crystals obtained in this way appear to be in all respects the same as they were before exposure to the rays. It would appear, therefore, that the reduction of the phosphorescent value is not primarily due to chemical change in the salt.

The fully developed crystalline condition of the yellow salt is evidently necessary, if the highest phosphorescence is to be obtained. Anything, therefore, which interferes with this condition impairs the phosphorescence.

8. When the water of crystallisation is wholly or partially expelled, the crystals, either yellow or red, are left in the form of an amorphous powder of a brick red colour. In this amorphous state the value of the phosphorescence has fallen to $2/100$ and the colour of the glow is no longer green but red. As crystals reddened by exposure to the β rays lose water and become opaque on heating to 130° just as the yellow crystals do, it may be concluded that the change from yellow to red under the influence of the β rays is not due to the loss of water of crystallisation.

9. As the reduction of the phosphorescent value in the change from the yellow to the red form is neither due to chemical decomposition nor to loss of water of crystallisation, it occurred to me that it might be akin to the change from the crystalline to the amorphous state,

* Rutherford, 'Radio-activity,' p. 168.

which had been observed in metals and other solids when they are flowed by mechanical movement.* The falling off of the phosphorescence under the long continued action of the rays suggested a failure in elasticity or elastic response analogous to that which is known in metals as "elastic fatigue," while the colour changes appear to be of the same nature as those observed in the crystalline and amorphous phases of the metals.†

10. When a small fragment of a yellow crystal is bruised on a glass plate by the rounded end of an agate pestle, the bright yellow colour is changed to deep red-brown wherever the pressure has acted so as to cause flow. This colour change is remarkably sharp and distinct. By rolling the pestle firmly over the smaller crystalline specks these are completely flowed into transparent patches with smooth rounded outlines. The colour of the thinnest patches is obviously more intense, as well as much redder, than that of the original crystal, while the thicker patches are of a very intense red-brown by transmitted light. The colour of the flowed patches by reflected light is complementary to that by transmitted light, being green. The crystalline structure of the yellow salt is to all appearance completely replaced by the vitreous granular structure of the amorphous phase.

11. A small quantity of the amorphous platino-cyanide was prepared by bruising and flowing the yellow crystals on a glass plate. With each portion the operation was repeated several times, that is to say, the flowed patches on the plate were scraped off, broken up and again rolled with the pestle. In this way, a fairly complete conversion into the amorphous form was obtained. The final product consisted partly of brown powder and partly of deep brown scales with a greenish sheen. The phosphorescence in the β rays was reduced to 2/100 of its value, and it appeared as a dull red glow in which an occasional speck of bright green indicated the presence of minute portions of the untransformed crystalline phase.

12. In my earlier observations on the phase changes $A \rightleftharpoons C$ ‡ it was shown that while the transformation $C \longrightarrow A$ takes place by mechanical movement of the molecules over each other, as in a liquid, the reverse transformation $A \longrightarrow C$ takes place only when a definite transition temperature or stability point is reached. The low temperature at which platino-cyanide loses its water of crystallisation presented a difficulty in attempting to bring about the transformation $A \longrightarrow C$ by heat, but an encouraging result was obtained on quickly raising a small portion of the amorphous salt to 85°, for the dark brown scales immediately assumed the bright greenish yellow of the

* 'Phil. Mag.,' vol. 8, 1904, pp. 258—276.

† *Ibid.*, also 'Roy. Soc. Proc.,' vol. 72, pp. 218—235.

‡ *Loc. cit.*

crystalline phase. The reality of this change was further confirmed by finding that the phosphorescent quality, which had fallen to 2/100 in the amorphous state, had been restored by the heating to 33/100.

13. The analogy between the changes in colour and phosphorescent quality brought about by the transformation $C \longrightarrow A$ and the corresponding changes which result from the action of the β rays is thus shown to be very close; it remained to be seen if the analogy also held good in the reverse transformation by heat.

14. Crystals which had been reddened by the β rays were lightly crushed and quickly heated to 110° in a capillary tube with an open end. The colour of the salt became much paler and its phosphorescent quality was considerably increased. As the temperature necessary to bring about the transformation was also high enough to drive off some of the water of crystallisation, a fresh portion of lightly crushed red crystals was packed tightly into a capillary tube which was sealed off as close to the surface of the salt as possible. The tube was heated to 120° , when the transformation into the yellow salt took place quite sharply, beginning simultaneously at the middle and at one end of the tube and quickly spreading all over, the brown colour giving place to bright yellow. The transformation was carried out at 120° , so that no water in the liquid state can have taken part in it. After cooling, some minute drops of condensed water were visible on the inner surface of the tube. Necessarily, a corresponding portion of the salt must have parted with some of its water of crystallisation, but this did not affect the transformation of the remaining part. The phosphorescent quality was raised from the 8/100 of the red crystals to 33/100.

15. Even in the sealed tube, however, the conditions for the transformation $A \longrightarrow C$ are distinctly unfavourable to anything like a perfect conversion or the production of a uniformly crystalline material, therefore, the very definite results obtained, namely, the partial restoration both of colour and phosphorescence, are strongly confirmatory of the phase view of the change brought about by the β rays.

16. The retention by the reddened crystals of their crystalline form and transparency points to a persistence of a proportion of the crystalline phase side by side with the amorphous. Having regard to my earlier observations on phase transformation in overstrained crystals, this persistence of the C phase is quite to be expected. In the case of gold it was shown that even after severe and repeated beating of the metal in the form of the thinnest foil the crystalline structure could not be completely obliterated.* More recent observations on the flow of crystalline salts, which have not yet been published, fully confirm this point. These still further confirm the explanation of this fact offered in my former papers, namely, that the amorphous phase which is formed at all the moving surfaces of the crystalline units acts as an

* 'Phil. Mag.,' vol. 8, p. 263.

encasing medium which protects the crystalline elements from further disintegration. In the case of the platino-cyanide, the over-stimulation to which the vibrating molecules are subjected by the β rays during the preliminary stage of bright phosphorescence, results in a state analogous to that of elastic fatigue in vibrating metal wires or glass fibres. Up to a certain point this fatigue may be recovered from, that is to say, if the relative displacements of the molecules from their proper crystalline relations has not passed beyond a certain stage; but beyond this stage there is no power of self-recovery, and heat is required to endow the molecules with freedom of movement sufficient to enable them to return to their crystalline positions. This final stage of permanent fatigue or overstrain in the salt corresponds with the amorphous condition which results from mechanically produced flow.

17. The foregoing observations show that physical structure and molecular elasticity may play an important part in the initial stimulation of phosphorescence, but the persistence of phosphorescence, even in the purely amorphous form of the substance, seems to point to the necessity for a more general explanation of the phenomena of phosphorescence. I propose to deal with the more general aspects of the subject in a separate communication.

18. In the appended table the comparative phosphorescence of the various forms of platino-cyanide of barium is shown. The method used was to measure the distance from the radium at which the salt exposed on a tray of black paper became distinctly visible in the dark. The salt was observed by means of a simple microscope fixed over the tray. The intensity of the rays was taken to be inversely as the square of the distance of the radium from the phosphorescing salt.

Comparative Phosphorescence (that of the canary-yellow crystals being taken as 100).

	Phosphorescent value.	Reference to paragraph.
1. Yellow crystals	100	No. 2
2. " " after exposure to β rays for 8 hours....	8	" 4
3. The same for 44 hours	8	" 4
4. Red crystals (No. 3 above) after heating to 110° in open tube	27	" 14
5. Red crystals, after heating to 120° in sealed tube	33	" 15
6. Yellow crystals dehydrated at 130° ...	2	" 8
7. Yellow crystals flowed into amorphous scales	2	" 11
8. The same (No. 7) heated to 85° — 100°	33	" 12